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(19)

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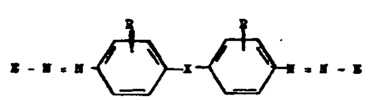
(54) CONCENTRATED AQUEOUS SOLUTIONS OF DISAZO DYES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SWIP 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fluid dyestuff compositions and more particularly to concentrated aqueous solutions of azo dyes.

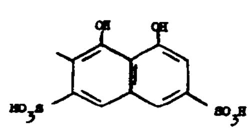
The use of concentrated aqueous solutions of dyes has gained favour in recent years because of the advantages they possess over dyes in powder form. Thus, the use of solutions avoids the problems associated with dust formation and frees the dye user from the time-consuming and often difficult task of dissolving the dye powder in water. The use of concentrated solutions has been further encouraged by the development of continuous dyeing processes for paper wherein it is convenient to meter the solution directly into the beater or some other suitable point in the paper manufacturing system.

The present invention provides a concentrated aqueous solution containing in 100 parts by weight of water, at least 8 parts by weight of an azo dye which, in the form of the free acid, has the formula:



(I)

wherein X represents an azoxy or azo linkage, R represents hydrogen, lower alkyl, lower alkoxy, sulpho or carboxy and E represents a radical of the formula:



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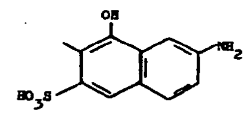
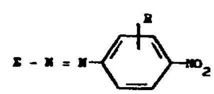


The terms "lower alkyl" and "lower alkoxy" used herein mean alkyl and alkoxy groups having from one to four carbon atoms.

The dyes of Formula I may be prepared by reducing a nitro monoazo dye of the formula:



(II)

wherein R and E have the meanings given above, using a method known to be capable of converting aromatic nitro compounds to azoxy or azo compounds. Such methods include the use of reducing sugars, for example D-glucose, in aqueous alkaline solutions.

Thus, the invention provides a concentrated aqueous solution containing 100 parts by weight of water, at least 8 parts by weight of an azo dye prepared by reducing a nitro monoazo dye of Formula II using an aqueous alkaline solution of a reducing sugar. The solution may be made alkaline by means of, for example, an alkali metal hydroxide or carbonate, ammonia or a mono-, di- or trialkanolamine.

The reduction is preferably performed by adding an aqueous solution of the reducing sugar (preferably between 0.5 and 1.5 mole per mole of nitro compound) to an aqueous solution of the nitro monoazo compound containing excess alkali metal hydroxide (up to 10 moles per mole of nitro compound) at temperatures between 50° and 100°C, preferably 75±2°C. The rate of the reduction may be controlled by adding the reducing sugar solution at such a rate that the redox potential measured between a platinum electrode and a calomel reference electrode is kept below 500 mV. Alternatively, the sugar solution may be

charged as rapidly as possible, the reduction being stopped when judged to be complete by the addition of acid.

The dye solution obtained from the reduction stage may be used as such or the dye itself may be isolated by conventional methods and then be re-dissolved in water. For maximum water-solubility, it is preferred to convert the dye, at least partially, into a lithium or a diethanolamine, or triethanolamine salt. Urea may be added to the dye solutions to provide even greater stability to storage.

The aqueous concentrates of the invention, which are stable to storage at temperatures as low as −5°C, are useful for the coloration of cellulosic materials, especially paper on which they give attractive blue shades with or without the use of size. The light-fastness of the dyed paper is significantly better than that of paper dyed with disazo dyes obtained from diamines such as benzidine and dianisidine with coupling components such as H-acid, Chicago acid and chromotropic acid.

An important feature of the dyes of Formula I is that their manufacture does not involve the use of intermediates known to be carcinogenic such as dianisidine.

The invention is illustrated by the following Examples in which all parts and percentages are by weight.

Example 1

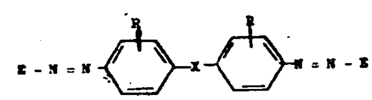
An aqueous suspension of a nitro-monoazo dye is formed by diazotisation of 2-methoxy-4-nitroaniline (16.8 parts) and coupling with 1,8-dihydroxynaphthalene-3,6-disulphonic acid (32 parts) in the presence of sodium acetate (23.6 parts) and 32% aqueous sodium hydroxide solution (14.8 parts). Sodium hydroxide (32% solution—87.5 parts) is added to the suspension and the temperature is raised to 75°±2°C forming a complete solution. A solution of D-glucose (13.6 parts) in water (150 parts) is rapidly added to the hot solution which is heated at 75°±2°C for a further 10 minutes after which time the reduction is judged complete by the absence of a violet outspread (nitro compound) when a sample is spotted onto filter-paper (Whatmans No. 1) and diluted with water. Hydrochloric acid (35.5%—47 parts) is then added to reduce the pH to 8.5 before the dyestuff is precipitated at 60°C by the addition of salt (125 parts). The dyestuff is isolated by filtration and the filter-cake washed with 5% brine. A concentrated aqueous solution of the dyestuff is formed by mixing the filter-cake with lithium hydroxide monohydrate (up to 5 parts) and water as necessary. Urea (45 parts) is then added to give a solution (460 parts) which after screening to remove traces of foreign matter is stable to storage, for at least several months. The dyestuff solution, containing at least 8 parts dye per 100 parts water, is suitable for dyeing paper pulp in the presence of rosin and alum size an attractive greenish-blue shade.

Example 2

A mixture consisting of an aqueous paste containing 1-hydroxy-2 - (4′-nitro-3-sulphophenylazo) - 7-aminonaphthalene-3-sulphonic acid (11.7 parts) prepared by diazotisation of 2-amino-5-nitrobenzene sulphonic acid and coupling onto 2-amino-8-hydroxynaphthalene-6-sulphonic acid in the presence of sodium carbonate), diethanolamine (80 parts) and water (100 parts) is heated to 75°±2°C forming a complete solution. A solution of D-glucose (3.4 parts) in water (35 parts) is added to the hot solution at such a rate that the redox potential measured between a platinum electrode and a calomel reference electrode is kept below 500mV. When the reduction is complete, as judged by T.L.C. analysis of a sample, the dyestuff solution is screened, urea (20 parts) and the water as necessary are added. The dyestuff solution, containing at least 8 parts dye per 100 parts water, is suitable for dyeing paper pulp in the presence of rosin and alum size an attractive reddish-blue shade.

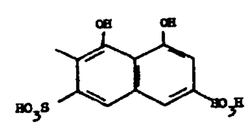
WHAT WE CLAIM IS:—

1. A concentrated aqueous solution containing in 100 parts by weight of water, at least 8 parts by weight of an azo dye which, in the form of the free acid, has the formula:



(I)

wherein X represents an azoxy or azo linkage, R represents hydrogen, lower alkyl, lower alkoxy, sulpho or carboxy and E represents a radical of the formula:



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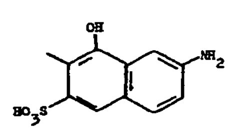
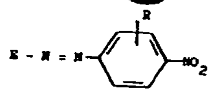


2. A concentrated aqueous solution as claimed in claim 1 wherein the azo dye is the product obtained by reducing a nitro monoazo dye of the formula:



(II)

using an aqueous alkaline solution of a reducing sugar.

3. A concentrated aqueous solution as claimed in claim 1 or claim 2 wherein the azo dye is in the form of a lithium, diethanolamine or triethanolamine salt.

4. A concentrated aqueous solution as claimed in claim 1 substantially as hereinbefore described with reference to either of the foregoing Examples.

5. A method of dyeing paper which uses a concentrated aqueous solution as claimed in any one of claims 1 to 4.

6. Paper dyed by the method of claim 5.

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